Explicitly Correlated Second Order Perturbation Theory with Frozen Gaussian-Type Geminals

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Abstract. We report on the performance of the explicitly correlated second order perturbation theory with frozen Gaussian-type geminals. Components in the Hylleraas energy functional are analyzed using the ansatz based on the *s*- and *p*-wave cusp conditions for singlet and triplet pairs. It is shown that calculated correlation energies are improved substantially by the introduction of the frozen geminals.

1   Introduction

In calculations with correlated methods, the basis set convergence is crucial for the predictions of reliable energetics and properties. It has been shown that enormous basis functions are required to achieve the chemical accuracy. This is the direct consequence of the inability of describing the Coulomb cusp[1] with one-electronic basis. To ameliorate this feature, various alternatives incorporating explicitly correlated functions have been proposed. The Gaussian-type geminals (GTGs)[2,3,4] have been used in many places. Especially, Szalewicz and coworkers introduced a novel alternative in the Hylleraas functional with the requirement of at most 3-electron integrals[5]. Although Gaussian-type functions never become exact for the cusp condition, the methods have shown the efficiency predicting correlation energy to an accuracy of $1\mu Eh$, as demonstrated by Cencek and Rychlewski[6] This situation is comprehensible by evaluating the motion of pair-electrons in the three-dimension space, *i.e.* the gain from the cusp around a fixed electron scales as $4\pi r_{12}^2$, vanishing at $r_{12} = 0$.

The R12 methods [7,8,9,10] developed by Kutzelnigg and coworkers utilize the linear r_{12} behavior with systematic approximations using the resolution of identity (RI) for bypassing the explicit treatment of 3- and 4-electron integrals. A large basis set is, however, required to guarantee the accuracy of RI with the non-vanishing ansatz. The long-range nature of the linear r_{12} behavior also makes a scalable treatment less straightforward. As a compromise between GTG and R12, Persson and Taylor proposed a method which fits the linear r_{12} behavior with GTG to avoid the nonlinear optimization[11]. The method aims at calculations of modest accuracy in comparison with the previous GTG theories, i.e. sub-*mEh* accuracy for valence

correlations within the framework of the second order many-body perturbation theory (MBPT2).

All of the above methods use explicitly correlated functions with orthogonal projectors and the Hylleraas energy functional. The transcorrelated method [12,13] of Boys and Handy is on the basis of a correlation factor independent of pairs. The similarity transformed Hamiltonian includes at most three-body effective interactions. Recently, we developed a new transcorrelated method with frozen GTG especially for pair-wise short-range collisions [14,15]. The method does not require any optimization of the correlation factor making use of the cusp condition. Instead, the long-range correlations are dealt with in terms of the usual configuration interaction (CI)-type expansion. In this paper, we study the second order Hylleraas energy functional of frozen GTG. When the geminals are universal for correlated pairs, the component of the kinetic energy operator is closely related to the transcorrelated Hamiltonian through the virial theorem. The effect of the p-wave cusp condition is also examined for triplet pairs. Numerical results are given in Sec. 3. and the conclusion is depicted in Sec. 4.

2   MBPT2 with Frozen GTG

Henceforward, we denote orthonormalized occupied and general orbitals in a given basis set as $ij\ldots$ and $pq\ldots$ respectively. In the GTG method, the second order energy is expressed as a sum of the usual MBPT2 energy and a correction in the Hylleraas energy functional outside the Hilbert space spanned by the given basis set,

$$E_V^{(2)} = E^{(2)} + \Delta E_V^{(2)} = E^{(2)} - \Delta E_N^{(2)} + 2\Delta E_Z^{(2)}, \tag{1}$$

$$\Delta E_N^{(2)} = \sum_{SM}\sum_{i \geq j} (c_{ij}^{(S,M)})^2 \left\langle \{ij\}^{(S,M)} \left| K_{12}^{(L)}(Q_1^* Q_2^* - Q_1 Q_2) f_{12} \right| \{ij\}^{(S,M)} \right\rangle, \tag{2}$$

$$\Delta E_Z^{(2)} = \sum_{SM}\sum_{i \geq j} c_{ij}^{(S,M)} \left\langle \{ij\}^{(S,M)} \left| r_{12}^{-1}(Q_1^* Q_2^* - Q_1 Q_2) f_{12} \right| \{ij\}^{(S,M)} \right\rangle, \tag{3}$$

where Q_n^* and Q_n are one-electron projectors in the virtual spaces for the complete and given basis sets, respectively, $\{ij\}^{(S,M)}$ denotes the spin-adapted antisymmetrized pair functions, $c_{ij}^{(S,M)}$ are variational parameters, and the operator, $K_{12}^{(L)}$, is an anti-hermite single commutator between the explicitly correlated geminal, f_{12}, and the kinetic energy operator,

$$K_{12}^{(L)} = [T_1 + T_2, f_{12}] = -(\nabla_1^2 f_{12}) - (\nabla_1 f_{12}) \cdot (\nabla_1 - \nabla_2), \tag{4}$$

f_{12} is expanded as a linear combination of spherically symmetric GTGs. The quantum numbers of the pair functions take the values, $(S,M) = (0,0)$, $(1,0)$, $(1,\pm 1)$ for $i \neq j$ and $(S,M) = (0,0)$ for $i = j$. The commutator involving the exchange operator is neglected in this particular work as in the MP2-R12/A ap-

proximation[9]. All three energy corrections become identical, $\Delta E_V^{(2)} = \Delta E_N^{(2)} = \Delta E_Z^{(2)}$, when the geminal is exact outside the orbital space,

$$(Q_1^* Q_2^* - Q_1 Q_2)(c_{ij}^{(S,M)} K_{12}^{(L)} + r_{12}^{-1}) \big| \{ij\}^{(S,M)} \big\rangle = 0, \quad \forall ijSM \ . \tag{5}$$

Thus the ratio,

$$\chi = \Delta E_Z^{(2)} / \Delta E_N^{(2)} \ , \tag{6}$$

which becomes unity in the above condition, is a good measure to indicate the appropriateness of geminals. It is possible to think of the connection between $\Delta E_V^{(2)}$ and $\Delta E_N^{(2)}$ as the virial theorem for the cusp condition. When $c_{ij}^{(S,M)}$ are coincident for all pairs, $\Delta E_N^{(2)}$ is directly obtained from the order-by-order expansion of the Schrödinger equation for the transcorrelated Hamiltonian [14]. In the transcorrelated method, the first order cusp condition in f_{12} is renormalized to infinite order in the similarity transformed Hamiltonian.

According to the analytical resolution,

$$Q_1^* Q_2^* = 1 - P_1 - P_2 + P_1 P_2 \ , \tag{7}$$

the functional is divided as

$$\Delta E_N^{(2)} = \Delta E_N^{(2)}[1] - \Delta E_N^{(2)}[P_1 + P_2] + \Delta E_N^{(2)}[P_1 P_2] - \Delta E_N^{(2)}[Q_1 Q_2] \ , \tag{8}$$

$$\Delta E_N^{(2)}[O] = \sum_{SM} \sum_{i \geq j} (c_{ij}^{(S,M)})^2 \big\langle \{ij\}^{(S,M)} \big| K_{12}^{(L)} O f_{12} \big| \{ij\}^{(S,M)} \big\rangle \ , \tag{9}$$

and a similar expression for $\Delta E_Z^{(2)}$. The component, $\Delta E_N^{(2)}[1]$, can be rewritten in the commutator form leading to the operator, $K_{12}^{(Q)}$, which appears in the transcorrelated method,

$$\Delta E_N^{(2)}[1] = \sum_{SM} \sum_{i \geq j} (c_{ij}^{(S,M)})^2 \big\langle \{ij\}^{(S,M)} \big| K_{12}^{(Q)} \big| \{ij\}^{(S,M)} \big\rangle \ , \tag{10}$$

$$K_{12}^{(Q)} = \frac{1}{2}[K_{12}^{(L)}, f_{12}] = -(\nabla_1 f_{12}) \cdot (\nabla_1 f_{12}) \ . \tag{11}$$

The term with single projectors reduces to 3-electron integrals and is approximated using RI of Kutzelnigg and Klopper[8], in the spin orbital basis as,

$$\big\langle ij \big| K_{12}^{(L)} P_1 f_{12} \big| kl \big\rangle \cong \sum_{mp} \big\langle ij \big| K_{12}^{(L)} \big| mp \big\rangle \big\langle mp \big| f_{12} \big| kl \big\rangle \ , \tag{12}$$

Since the 2-electron integrals in the RI expressions involve three occupied orbitals, the maximum angular momentum required in the RI basis becomes $3L_{occ}$ for the highest occupied angular momentum, L_{occ}, in an atomic calculation. Thus s-, f-, and i-functions contribute for systems with s-, p-, and d-occupied shells, respectively. Very

recently, making use of density fitting, we developed a novel decomposition scheme, which reduces the requirement to $2L_{occ}$ [16]. We do not employ the scheme in this work, focusing on molecules without d-occupied orbitals. The performance of the approximation is investigated using the index of RI,

$$\tau = \Delta E_N^{(2)}[P_1 + P_2] - 2\Delta E_Z^{(2)}[P_1 + P_2] + 4\Delta E_Z^{(2)}[P_1 P_2] \tag{13}$$

The term, $\Delta E_Z^{(2)}[P_1 P_2]$, dependent on the description of occupied orbitals has relatively large amplitude whereas $\Delta E_N^{(2)}[P_1 P_2]$ is zero because of the symmetry of the operator, $K^{(L)}$. The exact energy for a given basis and f_{12},

$$\bar{E}_V^{(2)} = E_V^{(2)} - \tau + \bar{\tau} \tag{14}$$

is estimated with a reliable $\bar{\tau}$ of an augmented basis set.

We bypass the optimizations of the parameters, $c_{ij}^{(S,M)}$, the coefficients and exponents of GTGs, using a template geminal, f_{12}^t, expanded as a linear combination of 10 Gaussians. It is determined in such a way that the Coulomb repulsion multiplied by a short-range weight Gaussian is suppressed in the similarity transformed Hamiltonian [14]. For the exponents, we use an even-tempered sequence in the range between 10^6 and 0.5 along with the weight Gaussian with the exponents, 5. f_{12}^t is further transformed with a scaling parameter, c_Z, as

$$f(r_{12}; c_Z) = c_Z^{-1} f^t(c_Z r_{12}). \tag{15}$$

Fig. 1 shows some profiles of $f(r_{12}; c_Z)$ with different scaling parameters. The effective radius of an explicitly correlated function is of c_Z with a template function whereas the approximate slope, $1/2$, is maintained around $r_{12} = 0$ by the scaling. As for the parameter, $c_{ij}^{(S,M)}$, Klopper developed a unitary invariant formulation to pair functionals in the MP2-R12 theory [17]. Such a convention is not employed in this work to keep the short-range behavior of f_{12}. Hence
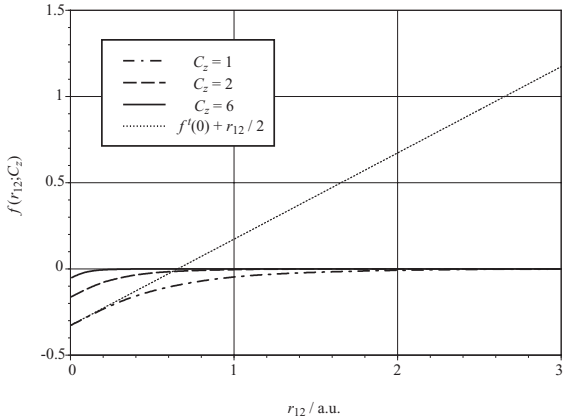

Fig. 1. Frozen geminals as functions of c_Z

we use $c_{ij}^{(0,0)} = 1$, for all singlet pairs. The triplet pairs $(S = 1)$ are antisymmetric in the spatial part to follow the p-wave cusp condition[18] and the parameters,

$c_{ij}^{(1,M)} = 1/2$, are used for the pairs. The latter condition is not crucial especially for
the use of a short-range geminal because of the Fermi hole at $r_{12} = 0$.

Table 1. Correlation energies of the Ne atom in mEh. All electrons are correlated

Basis set[b]	c_z	$\tau - \overline{\tau}$ [a]	χ	$E_V^{(2)}$	$\overline{E}_V^{(2)}$	$E^{(2)}$
VDZ	1.0	-41.05	0.82	-381.69	-340.6	-255.48
(9s4p1d)	2.0	-16.54	1.08	-351.25	-334.7	
	3.0	-7.89	1.24	-322.06	-314.1	
VTZ	1.0	-6.98	0.76	-377.39	-370.4	-321.93
(10s5p2d1f)	2.0	-3.58	0.98	-375.26	-371.7	
	3.0	-2.14	1.16	-364.33	-362.2	
VQZ	1.0	-1.52	0.75	-381.32	-379.8	-351.22
(12s6p3d2f1g)	2.0	-0.87	0.89	-382.86	-382.0	
	3.0	-0.63	1.06	-379.48	-378.9	
CVTZ	1.0	-5.40	0.86	-382.03	-376.6	-333.49
(12s7p3d1f)	2.0	-1.79	1.05	-374.46	-372.7	
	3.0	-0.91	1.19	-364.59	-363.7	
AVDZ	1.0	-27.45	0.80	-395.07	-367.6	-278.21
(10s5p2d)	2.0	-15.32	1.07	-371.26	-355.9	
	3.0	-7.66	1.23	-343.51	-335.9	
AVTZ	1.0	-3.20	0.75	-381.83	-378.6	-330.17
(11s6p3d2f)	2.0	-3.24	1.12	-382.35	-379.1	
	3.0	-2.06	1.14	-371.64	-369.6	
ACVQZ[c]	1.0	-13.43	0.97	-399.84	-386.4	-320.08
(16s10p6d)	2.0	-5.60	1.32	-373.57	-367.9	
	3.0	-2.44	1.53	-354.50	-352.1	
ACVQZ[c]	1.0	0.00	0.89	-387.55	-387.5	-354.94
(16s10p6d4f)	2.0	0.00	1.12	-382.35	-382.4	
	3.0	0.00	1.29	-375.56	-375.6	
ACVQZ[c]	1.0	0.00	0.85	-387.14	-387.1	-365.91
(16s10p6d4f2g)	2.0	0.00	1.00	-386.08	-386.1	
	3.0	0.00	1.17	-382.69	-382.7	
Limit						-388.1[d]

[a] The reference values of the index, $\overline{\tau}$, are based on the calculations with the aug-cc-pCVQZ
(uncontracted) set. It takes the values, 1354.27, 447.03, and 200.98 *mEh* for c_z =1.0, 2.0, and
3.0, respectively.
[b] The uncontracted set of the primitives in cc-p(C)VXZ and aug-cc-pCVXZ sets.
[c] Angular subcomponents of the reference primitive set, ACVQZ (uncontracted).
[d] A estimate value in the MBPT2 limit taken from Ref.[1].

3   Results and Discussions

Table 1 shows the results of the Ne atom with the uncontracted functions in the
correlation consistent basis sets [20,21]. We took the reference value of the RI index,
$\overline{\tau}$, from the calculations with aug-cc-pCVQZ (uncontracted) set, which is sufficiently
accurate to ca. 0.2mEh [16]. The errors in RI, $\tau - \overline{\tau}$, are significant especially for the

use of a small basis set and a large c_z. The positive increment of $E_V^{(2)}$ with $c_z = 1$ from VDZ to VTZ is mostly an artifact of the insufficiency of the DZV set, in which the f-shells are absent. The energy, -399.84 mEh, in the calculation of $(16s10p6d)$ and $c_z = 1$ is also lower than the MBPT2 limit by ca. 12 mEh artificially. It is preferable to use the decomposition scheme with density fitting to bypass the requirement of the f-shells[16]. The slightly positive increment from $(16s10p6d4f)$ to $(16s10p6d4f2g)$ is due to the neglect of the commutator between the exchange and geminal operators since the augmentation of the g-shell does not affect the accuracy of RI.

The electron correlation is a short-range phenomenon. Thus the calculation with VXZ sets shows that the results become less sensitive to the choice of c_z with the increase of the cardinal number, X. The series of ACVQZ shows quite different behavior; the estimated energy, $\bar{E}_V^{(2)}$, is almost saturated at the d-shell and is less sensitive to the augmentation of angular functions at $c_z = 1$. In the difference between VTZ and CVTZ, the results with $c_z = 2$ and 3 are hardly altered whereas there is an improvement, ca. 5mEh for $c_z = 1$. This implies that the geminal with a large radius is inappropriate for correlations concerning core electrons and the situation is improved significantly by the augmentation of the core correlation functions.

Table 2. MBPT2 energies (in *mEh*) of some typical molecules computed with the cc-pVTZ basis set (uncontracted) and $c_z = 2$

Molecule	χ	$E^{(2)}$	%	$E_V^{(2)}$	%	Limit[a]
CH_2	1.00	-183.79	87.6	-202.15	96.3	-209.9
CH_4	1.05	-243.89	89.1	-265.34	97.0	-273.6
NH_3	1.05	-283.32	87.7	-310.81	96.3	-322.9
H_2O	1.06	-318.46	87.9	-347.45	96.0	-362.1
HF	1.01	-326.07	84.8	-370.27	96.3	-384.6
Ne	0.98	-321.93	83.0	-375.26	96.7	-388.1
CO	1.02	-450.42	86.7	-501.71	96.5	-519.7
N_2	1.02	-469.31	87.4	-518.20	96.5	-536.9
F_2	1.00	-630.61	85.1	-714.74	96.5	-740.6

[a] The values in the Refs. [19] and [22]

We show the calculated MBPT2 energies of some molecules with cc-pVTZ basis set (uncontracted) and $c_z = 2$ in Table 2. The conventional MBPT2 covers from 83% (Ne) to 89% (CH_4) of the correlation energies in the complete basis limits. In explicitly correlated calculations, the ratio, χ, is dependent on the choice of c_z and basis set as seen in the Ne result. It however ranges in a small area between 0.98 (Ne) and 1.06 (H_2O) irrespective of the system. Generally speaking, the error of RI reduces in the calculation of a molecule compared to atoms. The effects are thus estimated less than 1% (for Ne) in the correlation energy. The use of the frozen GTG reproduces ca. 96% of the MBPT2 energies reducing the correlation error by 2/3–3/4 compared to the conventional expansion.

4 Conclusion

We have illustrated the MBPT2 method with frozen GTG. Instead of minimizing the pair energy functional, the *s*- and *p*-wave cusp conditions are utilized in adapting the geminal. It is shown that the present method improves the calculation of MBPT2 energy substantially.

References

1.   T. Kato Commun. Pure Appl. Math. 10 (1957) 151
2.   S. F. Boys, Proc. Roy. Soc. London Ser. A258 (1960) 402
3.   K. Singer, Proc. Roy. Soc. London Ser. A258 (1960) 412
4.   K.-C. Pan and H. F. King, J. Chem. Phys. 56 (1972) 4667
5.   K. Szalewicz, B. Jeziorski, H. J. Monkhorst and J. G. Zabolitzky, J. Chem. Phys. 78 (1983) 1420
6.   W. Cencek and J. Rychelewski, Chem. Phys. Lett. 320 (2000) 549
7.   W. Kutzelnigg, Theor. Chim. Acta. 68 (1985) 445
8.   W. Kutzelnigg, W. Klopper, J. Chem. Phys. 94 (1991) 1985
9.   V. Termath, W. Klopper and W. Kutzelnigg, J. Chem. Phys. 94 (1991) 2002
10. W. Klopper and W. Kutzelnigg, J. Chem. Phys. 94 (1991) 2020
11. B. J. Persson, P.R. Taylor, J. Chem. Phys. 105 (1996) 5915
12. S. F. Boys and N. C. Handy, Proc. R. Soc. A 310 (1969) 43
13. N. C. Handy, Mol. Phys. 26 (1973) 169
14. S. Ten-no, Chem. Phys. Lett. 330 (2000) 169; *ibid*. 330 (2000) 175
15. O. Hino, Y. Tanimura and S. Ten-no, J. Chem. Phys. 115 (2001) 7865; O. Hino, Y. Tanimura and S. Ten-no, *Chem. Phys. Lett.* 353 (2002) 317
16. S. Ten-no and F. R. Manby, J. Chem. Phys., to appear. (2003)
17. W. Klopper, Chem. Phys. Lett. 186 (1991) 583
18. V. A. Rassolov and D. M. Chipman, J. Chem. Phys. 104 (1996) 9908
19. W. Klopper and C.C. M. Samson, J. Chem. Phys. 116 (2002) 6397
20. T. H. Dunning, Jr., J. Chem. Phys. 90 (1988) 1007
21. D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. 103 (1995) 4572
22. "CC-R12: An Explicitly Correlated Coupled-Cluster Theory", J. Noga, W. Klopper and W. Kutzelnigg, in R. J. Bartlett (ed) "Recent Advances in Coupled-Cluster Methods" World Scientific (1997)